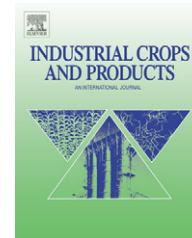


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Properties of dry film lubricants prepared by spray application of aqueous starch–oil composites[☆]

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ABSTRACT

Aqueous dispersions of starch–soybean oil (SBO) and starch–jojoba oil (JO) composites, prepared by excess steam jet cooking, form effective dry film lubricants when applied as thick coatings to metal surfaces by a doctor blade. This application method necessitates long drying times, is wasteful, requires the addition of sucrose to promote composite adhesion to the metal surface, and restricts the substrate geometry to planar surfaces. These issues represent important barriers to the commercialization of this aqueous biobased dry film lubricant technology. We now report an air-assisted spray method that uses readily available spray equipment to apply aqueous starch–oil composite dispersions as thin coatings (0.15–2.0 mg/cm²) to metal surfaces quickly and efficiently. Aqueous dispersions of waxy maize starch–oil composites containing either SBO, JO or hexadecane (HD), having 0.020–31.7 wt% oil relative to starch, were applied by air-assisted spraying and could be dried to the touch in approximately 30 s. Additionally, sucrose was found unnecessary for adhesion of the sprayed coatings. Tribological ball-on-flat testing of metal specimens spray coated with starch–SBO, –JO, and –HD composites showed the thin films of starch–SBO and –JO performed better at reducing the coefficient of friction (COF) than the starch–hexadecane composites. A low COF ranging between 0.027 and 0.044 was obtained for the starch–SBO and –JO composites containing 4–5 wt% oil relative to starch. Above 4–5 wt% oil loadings, no further COF reductions were realized. Further results revealed that micrometer-sized oil droplets embedded within the dried starch matrix of the composite film are delivered “on demand”. It appears that when pressure is applied to the dry film lubricant, the starch matrix ruptures and releases the entrained oil to the friction surface.

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1. Introduction

Lubricants are widely used in manufacturing processes to protect product surface quality, optimize the coefficient of friction (COF) for fabrication processes, and to reduce tool wear (Wang, 2004). Sheet metal forming processes are among

the most important metal-working operations for which large quantities of liquid lubricants are used. These lubricants are generally petroleum-based and contain environmentally harmful chemical additives and are collected after use as waste oils to be partially recycled or burned (Wagner et al., 2001).

[☆] Product names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may be suitable.

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Because of health, economic and environmental issues, a revival in the development of biobased lubricants from renewable resources is ongoing as agriculturally based materials are generally considered non-toxic, easily biodegradable, and abundantly available (Canter, 2001; Isbell et al., 2006; Legrand and Durr, 1998; Mang, 1994, 1997). In addition to liquid biobased lubricants derived from unmodified and modified vegetable oils, dry film biobased lubricants are of interest because they can enhance the formability of bare sheet metal and can provide corrosion protection and scratch resistance during transport and handling. Also, since dry film lubricants can be efficiently distributed, less lubricant is typically needed (Meiler et al., 2003).

Stable starch–lipid composites can be prepared by co-jet cooking mixtures of starch and lipophilic materials such as vegetable oils under excess steam conditions (Eskins and Fanta, 1997, 1999; Fanta et al., 1999). Steam jet cooking represents a convenient and inexpensive process to prepare aqueous starch dispersions for industrial applications (Klem and Brogly, 1981; Schroyer, 1997). These composites are water dispersible over a wide range of dilution and microscopic analyses have shown the composites to consist of lipid droplets having typical diameters in the 1–10 μm range coated with a thin film of firmly bound starch at the lipid–water interface (Fanta and Eskins, 1995; Eskins et al., 1996; Fanta et al., 1999). Aqueous dispersions of starch–oil composites can be drum dried and milled to produce powdered starch–oil composites that are easily reconstituted in water to form smooth, stable dispersions.

Aqueous dry film lubricant formulations containing starch–SBO composites and sucrose were applied to steel plates as thick films and the boundary COF and wear properties were evaluated (Biresaw and Erhan, 2002; Biresaw, 2004; Biresaw et al., 2007). Sucrose was required in these formulations to promote adhesion to the metal substrates, plasticize the thick films, and prevent cracking. The COF measured for these formulations was dependent upon the starch:SBO ratio, and as the SBO content in the composite increased, COF decreased asymptotically.

An important criterion for commercialization of aqueous starch–oil composites as dry film lubricants is their application to metal surfaces in a cost effective manner. In past studies, the dry film lubricant formulations were applied by first pouring the aqueous composite onto the metal substrate, spreading the formulation using a doctor blade and then allowing the coating to dry for a minimum of 24 h before testing the COF. Although this technique was adequate for conducting the initial scientific investigations, commercial application of the dry film lubricant formulations in this manner is inefficient and wasteful. Additionally, the presence of sucrose in the formulation is undesirable as it may promote moisture retention in the coating that could promote oxidation.

To address these shortcomings, we developed an air-assisted spray method, and performed microscopic analyses, and tribological evaluations of the resulting films. A series of waxy maize starch–oil composites containing various amounts of either soybean oil (SBO), jojoba oil (JO) or hexadecane (HD) were prepared by excess steam jet cooking. Aqueous dispersions of the composites (with and without sucrose) were applied to metal surfaces quickly and efficiently using readily

available spray equipment. The resulting coatings were evaluated for their drying time, surface coverage and tribological properties relative to previous studies that examined thicker sucrose containing films of starch–SBO composites applied by a doctor blade. Analysis of the surface oils on the coatings provided insight into how these starch–oil composites provide lubrication to surfaces as dry film lubricants.

2. Experimental

2.1. Materials

Soybean oil and sucrose were purchased from a local supermarket. Jojoba oil was obtained from the New Crops and Processing Technology Research Unit at USDA-NCAUR (Peoria, IL). Waxy cornstarch (Waxy No. 1) was obtained from A.E. Staley Mfg. Co. (Decatur, IL). Hexadecane was purchased from Sigma–Aldrich (St. Louis, MO). Deionized distilled (DI) water was used for all experiments. Type 304, 0.076 cm \times 30.48 cm \times 30.48 cm steel plates were obtained from McMaster Carr Supply Co. (Elmhurst, IL) and cut into 7.8 cm \times 15.4 cm specimens for use in friction experiments. Grade 100, 440-C stainless steel balls were obtained from Altek Co. (Torrington, CT) and had the following specifications: diameter, 15.88 \pm 0.02 mm; sphericity, 0.0254 mm; hardness, 57–67 c. The steel balls and plates were cleaned by sonications in DI water (5 min), acetone (2 min), and hexane (2 min) and then air dried.

2.2. Starch–lipid composite preparation

In a typical preparation, a mixture of waxy starch (1101.2 g, moisture content 10.3%) was added to DI water (2000 ml) and stirred in a 4 l stainless steel Waring blender (model 37BL84; Dynamics Corporation of America, New Hartford, CT). The resulting slurry was delivered to the jet cooker utilizing a Moyno progressive cavity pump (Robbins Meyers, Springfield, OH) at a flow rate of about 1 l/min. The starch slurry and steam were combined in a Penick and Ford hydroheater (Penford Corp., Cedar Rapids, IA). Cooking temperature was 140 $^{\circ}\text{C}$ using steam supplied at 550 kPa (65 psig), and the hydroheater backpressure set at 377 kPa (40 psig). The cooked starch solution was collected along with additional steam heated water to obtain a total volume of 5000 ml (solids content: 19.18 \pm 0.04%, as determined by freeze-drying accurately weighed amounts of the dispersion in duplicate). To a portion of the starch solution (2001.4 g, containing 383.8 g starch), SBO (38.90 g) was added and the mixture blended at high speed in a Waring blender for approximately 2 min. This oil–starch suspension was then fed through the jet cooker under the conditions previously described. A center cut (approximately 1500 ml) of the white opaque dispersion was collected from the jet cooker and subsequently drum dried on a pilot-scale double drum dryer (model 20; Drum Dryer and Flaker Company, South Bend, IN) heated with steam at 308 kPa (30 psig) (135 $^{\circ}\text{C}$) to give white composite flakes. The flakes were subsequently milled to a fine powder using a rotary beater mill (Model ZM 200; Retsch Inc., Newtown, PA) operating at 300 Hz (18,000 RPM). The theoretical SBO concentration in the composite relative to

Table 1 – Starch–oil composites prepared from waxy starch and either SBO, JO, or HD

Starch–oil composite	Oil used (g)	Starch used (g)	Percent oil (%) ^a	Percent starch (%) ^a	Oil:starch (pph) ^b	COF ^c
SBO						
1	0.068	401.46	0.020	99.98	0.020	0.697 ± 0.033
2	0.41	401.20	0.10	99.90	0.10	0.571 ± 0.063
3	1.22	401.34	0.30	99.70	0.30	0.536 ± 0.033
4	1.77	401.24	0.44	99.56	0.44	0.395 ± 0.028
5	3.74	401.40	0.92	99.08	0.93	0.283 ± 0.037
6	4.98	401.60	1.22	98.78	1.24	0.180 ± 0.003
7	6.32	378.13	1.64	98.36	1.67	0.120 ± 0.003
8	7.63	377.98	1.98	98.02	2.02	0.097 ± 0.015
9	8.90	378.06	2.30	97.70	2.35	0.099 ± 0.004
10	10.64	378.04	2.74	97.26	2.82	0.069 ± 0.009
11	11.48	378.04	2.95	97.05	3.04	0.081 ± 0.002
12	19.40	378.06	4.88	95.12	5.13	0.044 ± 0.004
13	27.18	383.81	6.61	93.39	7.08	0.058 ± 0.004
14	38.90	383.87	9.20	90.89	10.13	0.046 ± 0.002
15	75.25	383.96	16.39	83.61	19.60	0.032 ± 0.002
16	178.10	384.04	31.68	68.32	46.38	0.033 ± 0.002
JO						
1	0.71	389.82	0.02	99.98	0.020	0.635 ± 0.074
2	0.40	390.18	0.10	99.90	0.10	0.668 ± 0.046
3	1.25	390.06	0.32	99.68	0.32	0.552 ± 0.046
4	1.62	390.20	0.41	99.59	0.41	0.589 ± 0.111
5	4.72	390.41	1.19	98.81	1.21	0.113 ± 0.002
6	8.58	385.48	2.18	97.82	2.23	0.052 ± 0.001
7	19.06	385.64	4.71	95.29	4.94	0.027 ± 0.004
8	37.98	396.75	8.74	91.26	9.57	0.026 ± 0.001
9	177.12	396.47	30.88	69.12	44.67	0.028 ± 0.002
HD						
1	3.70	382.13	0.96	99.04	0.97	0.608 ± 0.036
2	7.56	408.14	1.82	98.10	1.85	0.415 ± 0.011
3	10.64	408.18	2.54	97.46	2.61	0.450 ± 0.043
4	11.41	408.86	2.71	97.29	2.79	0.568 ± 0.052
5	19.37	408.45	4.53	95.47	4.74	0.395 ± 0.011
6	27.38	379.74	6.73	93.27	7.21	0.417 ± 0.002
7	40.40	379.82	9.61	90.39	10.64	0.330 ± 0.058
8	74.57	379.89	16.41	83.59	19.63	0.217 ± 0.025
9	177.35	379.82	31.83	68.17	46.69	0.335 ± 0.072

^a Percent oil = oil used (g)/(oil used (g) + starch used (g)); percent starch = starch used (g)/(oil used (g) + starch used (g)).

^b pph = parts per hundred, expressed as (oil (g)/starch (g))*100 dry weight basis of starch.

^c Average of three runs.

starch was 9.2%. Expression of the SBO concentration in parts per hundred (pph) relative to dry starch = $(38.90 \text{ g SBO}/383.8 \text{ g starch}) \times 100 = 10.1 \text{ pph}$. Other starch–SBO, –JO and –HD composites were prepared similarly as described, Table 1.

2.3. Formulation of starch–oil composites for dry film lubricant spray application

The drum dried starch–oil composites were reconstituted at rt DI water utilizing a Waring blender. The formulation of a starch–SBO composite that contained 9.2 wt% SBO and 90.8 wt% starch is representative. To a DI water (236 ml) sucrose (15 g) solution stirred in a Waring blender at low speed, the dried composite (22 g, contained 19.99 g starch) was added slowly. The mixture was then blended at high speed for 4–5 min to form a homogenous dispersion. The final starch and sucrose concentrations in the formulation were 8.5 and 6.4 wt%, respectively. The starch–SBO composites

without sucrose, containing 16.4 wt% SBO, aqueous formulation was prepared using 22.0 g of composite and 217 ml of DI water. The composite was prepared in a Waring blender as described above and used immediately. To maintain similar viscosities between starch and oil composites having different starch:oil ratios, the amount of water was adjusted to maintain the starch concentration at 8.5 wt%. Because the amount of sucrose (15 g) in each formulation was not adjusted, the sucrose concentration within each starch–oil composite series ranged between 5.7 and 8.4 wt%. The formulations were used immediately after preparation.

2.4. Air-assisted spray application of aqueous dry film lubricant formulations

A Badger Model 400 detail/touch-up siphon feed spray gun (Badger Air-Brush Co., Franklin Park, IL) with a medium spray needle valve tip (0.85 mm) and vertical fan pattern spray

nozzle was operated at 207 kPa (30 psi). The fan spray height and width was approximately 5–6 cm \times 2 cm at a distance of 10 cm. The metal specimen was placed vertically at a slight angle and the aqueous dry film lubricant formulation was applied by spraying parallel to the metal surface at a distance of approximately 13–18 cm. The spray gun was moved from left to right and back again while moving progressively down the plate. This process was repeated until the desired surface coverage of the coating was obtained. The drying times were measured by monitoring weight loss during evaporation. Surface coverage was determined gravimetrically.

2.5. Microscopy

Composite films sprayed onto standard glass microscope slides were examined and photographed with a Zeiss Axioskop microscope (Carl Zeiss Inc., Thornwood, NY) using phase contrast optics. Tracks formed by the 3-ball test sled on the metal specimens were photographed with low angle incident light using a Zeiss Stemi 2000-C dissecting microscope.

Film thickness was determined using a microscope slide which had been sprayed so as to bear 0.61 mg/cm² of material. A standard coverslip was measured with a precision micrometer and determined to be 150 μ m thick (well within commercial specifications). By focusing alternatively on ink markings applied to the top and bottom of the coverslip using a dry 40 \times objective, the stage height fine focus knob rotation scale was calibrated to 1.80 μ m/unit. A razor blade was used to cut and scrape portions of the film from the microscope slide. By focusing alternatively on the top of the applied film and the adjacent microscope slide surface, the film thickness was determined to be 15.94 μ m.

2.6. High performance liquid chromatography. Analyses for SBO on coating surface

SBO contained on the surface of the spray applied dry film lubricant coating was removed from the coating surface by gently wiping a hexane soaked piece of absorbent towel (2 cm \times 2 cm) using tweezers across the entire surface of a metal plate coated with starch–SBO composites. The towel was then placed into an HPLC vial and 1.5 ml of hexane was added. The oil removal process was repeated eight times per metal plate. The SBO extracted by the towel was then analyzed by normal phase HPLC on a Dynamax (250 mm \times 4.6 mm, 60 \AA , 8 μ m) silica column (Varian, Walnut Creek, CA). A 20 μ l injection of sample was eluted from the column with a hexane/acetone 80:20 mixture at 1 ml/min with the ELSD drift tube set at 55 $^{\circ}$ C and nebulizer set at 138 kPa (20 psi) N₂. SBO had a retention time of 2.82 min. To investigate the release of additional oil from the film due to the pressure of the test sled moving over the film, several coated metal specimens were subjected to 36 passes of the COF measurement procedure, with repositioning of the specimen between passes to minimize sled track overlaps.

2.7. Coefficient of friction measurements

COF data was measured as previously described (Biresaw and Erhan, 2002) utilizing a ball-on-flat test geometry on an instru-

ment constructed by combining the SP-2000 slip/peel tester from Imas, Inc. (Accord, MA) and the Model 9793A test weight sled from Altek Co. (Torrington, CT). A flat metal specimen coated with the desired lubricant was secured to the platen was pulled from under a 1500 g sled connected to a load cell. This sled had three metal balls installed in the bottom contacted the lubricant covered sheet. The load cell, with a range of 0–2000 g, measured the friction force resisting the movement of the sled. The COF was obtained by dividing the measured friction force by the weight of the sled. All friction experiments were conducted at room temperature, using a platen speed of 2.5 mm/s for a total test time of 20 s. Three sheet metal specimens were prepared for each dry film lubricant formulation, and triplicate tests were conducted on each metal specimen. Between runs on the same metal sheet, the three balls were wiped with an acetone soaked Kimwipe[®] and rotated. The balls were replaced with clean new balls between sheets with lubricants of different oil concentrations.

3. Results and discussion

3.1. Starch–lipid composite preparation

Composites were prepared by excess steam jet cooking aqueous mixtures of waxy cornstarch with each of the lipophilic components SBO, JO, or HD. The amounts of oil and starch used to prepare the various starch–oil composite samples in the series are given in Table 1, as well as the final lipid and starch amounts contained in each of the composites. As can be seen, the percentage of oil contained in the composites (column 4, Table 1) ranged between approximately 0.02 and 32% for each starch–oil composite series (SBO, JO, HD) and represented typical lipophilic loadings for applications utilizing the starch–oil composites. Alternatively, the amount of oil in the composites can also be expressed in parts per hundred (pph) relative to dry basis waxy starch, and ranged from 0.02 to 47 pph (Table 1, column 6). The oil droplet sizes in the composites ranged in diameter from 1 to 10 μ m. The composites exhibited physical characteristics similar to those previously reported (Eskins et al., 1996; Fanta et al., 1999). The aqueous starch–oil composites were subsequently drum dried into flakes and milled to give powders that readily dispersed in water when blended using a Waring blender.

3.2. Preparation and air-assisted spray application of aqueous based dry film lubricant formulations containing sucrose

To determine whether the thin films of the starch–oil composite dry film lubricants that were air-sprayed onto metal surfaces reduced COF as effectively as the coatings previously applied with doctor blades (Biresaw and Erhan, 2002), sucrose was included in the aqueous dispersions of the starch–oil composites. Sucrose was required in the earlier formulations to promote adhesion and flexibility to the thicker composite coatings since these coatings prepared without sucrose cracked and peeled off the metal surfaces (Biresaw and Erhan, 2002). In the present study, the sucrose concentration in the aqueous dry film lubricant formulation was maintained

between 5.7 and 8.4 wt% and was within the ranges reported previously (Biresaw and Erhan, 2002).

A siphon feed spray gun was used to apply the aqueous dispersions of starch–oil composites. A low volume flow of high pressure air was used to apply and to shape the pattern of the aqueous dispersion as it is discharged from the nozzle assembly.

The water used to formulate the composites within an oil series was adjusted so as to maintain the starch concentration at 8.5 wt% for each starch–oil composite. At this solids content, an air pressure of 207 kPa (30 psi) was found to effectively disperse and apply the composites to the metal substrates.

Dried coatings of the starch–oil composites prepared either with or without sucrose were translucent. Visual inspection of these coatings on the metal surfaces showed no observable cracking or peeling. Tilting the metal plate under light while observing the coating showed a slight orange peel texture suggesting the droplets hit the metal surface and dried before nearby droplets could fully coalesce. Scratching either of these coatings with a fingernail did not visibly mar the surface of the film. At no point during the investigation did the non-sucrose containing films show any cracking, peeling, or detachment from the substrate.

3.3. Microscopy of sprayed film

Phase contrast micrographs of very lightly sprayed, moderately sprayed, and heavily sprayed areas on a glass microscope slide are shown in Fig. 1(A–C). In very lightly sprayed areas, the droplets dried before any coalescence occurred, as indicated by the presence of oil droplets in every more or less circular dried film (Fig. 1A). Areas which received more spray coverage before drying showed evidence of coalescence, in that areas rich in oil droplets were observed which were continuous with areas with few or no oil droplets (Fig. 1B). These images were interpreted as resulting from the migration of freely mobile oil droplets in a continuous wet film into clusters, that on drying left areas which consisted only of dark grey appearing starch deposits. When sequential spray passes resulted in a heavier accumulation of material (Fig. 1C), it appeared that all areas of the film contained oil droplets in one or more layers, and no areas devoid of oil droplets were seen.

A photograph of a composite coated metal test specimen which was subjected to multiple passes of the COF measurement procedure is shown in Fig. 2A. The scrape pattern is barely visible in room lighting, but the tracks can be readily discerned when illuminated with a bright light with a low incidence angle to increase the contrast of the track against the reflective metal substrate. The microscopic image of the tracks similarly illuminated (Fig. 2B) indicated that the film was not removed by the passage of the test sled balls, but rather a variable delamination or flaking could be seen. It is assumed that the dried composite film possesses a degree of flexibility on the microscopic scale, and that sufficient stress and distortion occurred at the contact point to cause separation of the multiple film layers. These disrupted layers would result in more or less planar film fragments situated at larger angles than parallel with the bulk film surface which would explain the glistening or flaky appearance of the tracks compared with the undisturbed areas of the film.

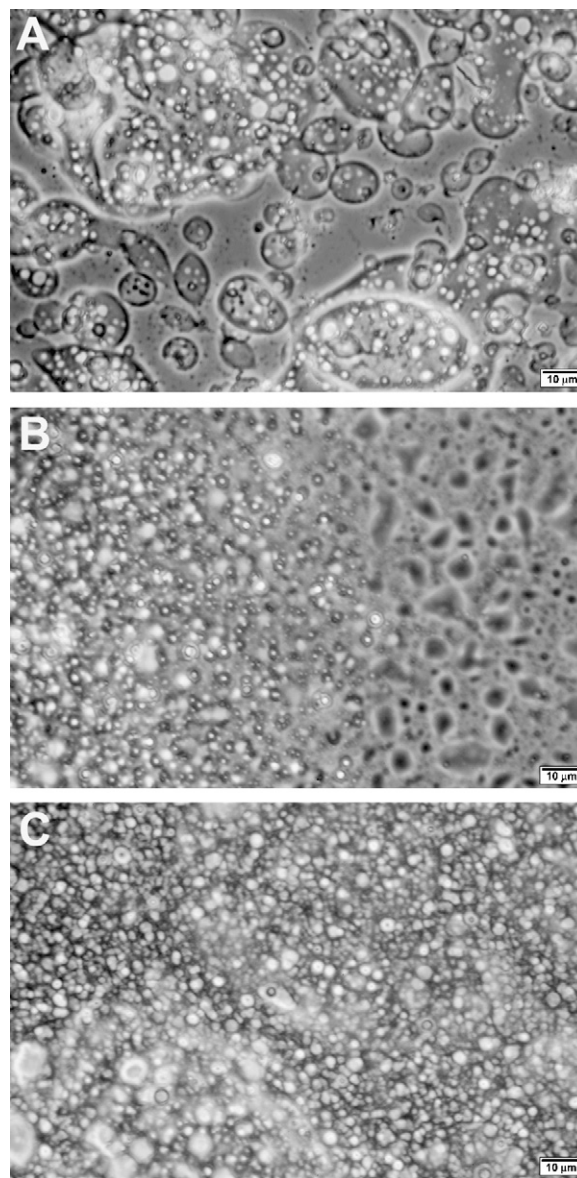


Fig. 1 – Phase contrast micrographs of very lightly sprayed (A), moderately sprayed (B), and heavily sprayed (C) areas on a glass microscope slide.

3.4. Drying times of sprayed starch–oil composite formulations on metal surfaces

In addition to the efficient spray application required for commercialization of these aqueous based dry film lubricants, the need for these formulations to dry quickly was also desirable. Because water has a relatively low evaporation rate, the drying times of thick coatings applied by a doctor blade required times up to 24 h for the water to evaporate (Biresaw and Erhan, 2002). Accordingly, we examined the drying times of sucrose containing composite formulations spray applied to metal substrates as thin coatings by following the weight loss over time of the coated metal sheets. The weight loss was attributed to evaporation of water from the coating as the oils and starch have minimal volatility. The coating weights

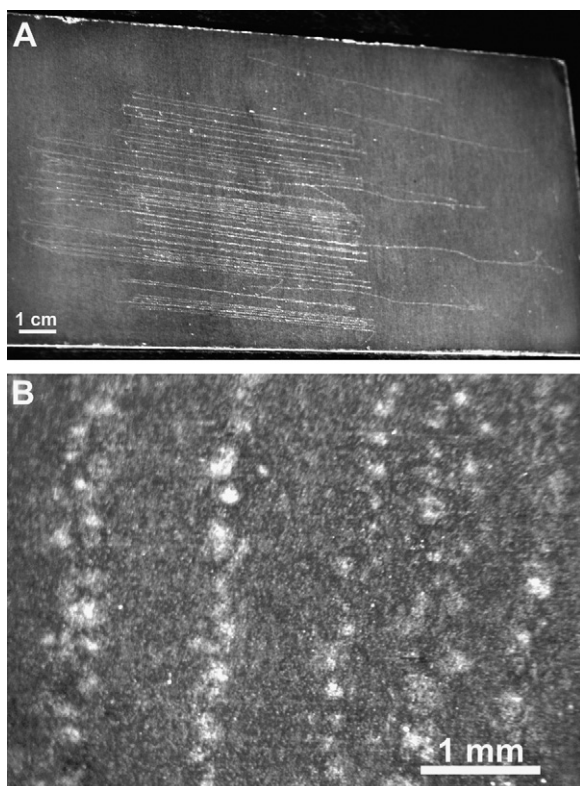


Fig. 2 – (A) photograph of a metal test specimen coated with spray applied starch-oil composite which was subjected to multiple passes of the COF 2 kg test sled. (B) The microscopic image of the tracks similarly illuminated.

were found to be stable after 10 min of bench-top drying with no heat or other external assistance was applied to dry the coatings. At this time the film was dry to the touch with no noticeable tackiness. To further reduce drying times of the sprayed formulations, a forced air drying system was tested. In this method, the coating was sprayed onto the metal sheet and immediately exposed to a gentle stream of cool air from a drying gun for approximately 30 s. Under these circumstances, at coating surface coverages similar to those studied for the bench-top dried samples, the coatings were dry to the touch immediately after removal from the forced air stream and showed no noticeable changes in the weight over time.

3.5. Tribological characteristics of starch-oil composites

Starch-oil composites containing sucrose were spray applied to metal surfaces to produce coatings having surface coverages ranging from 0.15 to 0.50 mg/cm². It was of interest to determine if these thin coatings provided COF reductions needed for dry film lubricant applications. The frictional forces were measured using a ball-on-flat test configuration and then divided by the test load (sled weight) to obtain the coatings corresponding COF. Fig. 3 shows several friction force profiles for the thin starch-SBO composites films containing sucrose.

As the percentage of SBO contained in the composite increased (profiles A–F, Fig. 3) the corresponding frictional

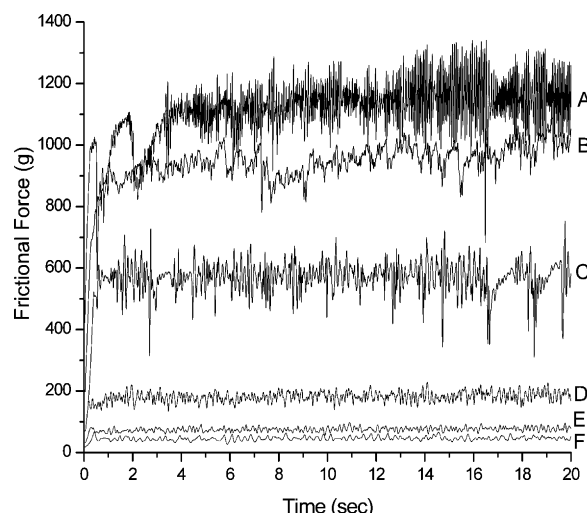


Fig. 3 – Representative frictional force profile data for various starch-SBO composites containing sucrose and spray applied to metal surfaces. (A) 0.02 wt% SBO in composite (0.34 mg/cm²); (B) 0.10 wt% SBO in composite (0.30 mg/cm²); (C) 0.44 wt% SBO in composite (0.25 mg/cm²); (D) 1.64 wt% SBO in composite (0.28 mg/cm²); (E) 4.88 wt% SBO in composite (0.38 mg/cm²); (F) 16.39 wt% SBO in composite (0.26 mg/cm²).

force decreased. As can be seen, at relatively low SBO loadings in the composite (4.88 wt% SBO; profile E in Fig. 3) the frictional force was effectively reduced to low values. Coatings prepared from composites containing higher loadings of SBO did not significantly reduce the frictional force beyond that of the 4.88 wt% SBO loaded composites.

Fig. 4 shows the average COF versus oil concentration determined for each of the dry film lubricant formulations tested for each oil series.

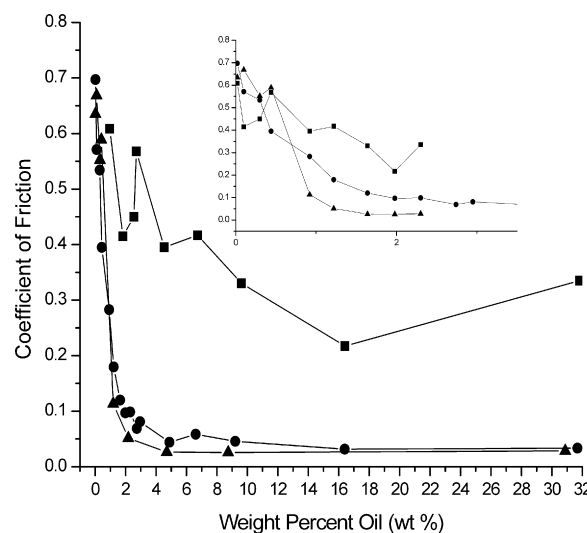


Fig. 4 – Effect of concentration on the COF of starch-oil composites. ■ = starch-HD composites; ● = starch-SBO oil composites; ▲ = starch-JO oil composites.

Although the COF for the sucrose containing SBO, JO, and HD composites decreased as the percentage of oil contained in the composite increased, the SBO and JO loaded composites showed dramatic decreases in the COF relative to HD composites. The hexadecane containing composites did not lower COF very well indicating that HD had poorer lubricity properties than the SBO and JO composites. This observation concerning lubricity follows the general trend noted by others (Knothe and Steidley, 2005) and can be ascribed to the differences between the nonpolar nature of HD and the polarity imparting oxygen atoms of the SBO and JO ester moieties.

3.6. Evaluation of spray applied aqueous based dry film lubricant formulations without sucrose

Because sucrose was not needed to promote adhesion, and its presence may promote moisture retention in the coating which could be detrimental to the metal surface, its exclusion from these coatings was desirable. To examine the properties of the starch–oil composite coatings without sucrose, the 16.4 wt% starch–SBO composite was further investigated.

Accordingly, the aqueous starch–SBO composite was sprayed onto metal sheets and dried with a cool air stream as previously described. The coatings dried to the touch within 30 s and three different surface coverages, 0.224 ± 0.010 , 0.421 ± 0.030 , and 0.529 ± 0.030 mg/cm² ($n = 3$), were prepared. The COF values were determined for these coatings and found to be 0.031 ± 0.002 , 0.029 ± 0.001 , and 0.042 ± 0.001 , respectively. From these results, it can be seen the COF values for the non-sucrose containing composite have similar reductions in COF as the sucrose containing composites (COF = 0.032 ± 0.002 , Table 1, entry 15 under SBO).

3.7. Determination of oil contained on coating surface

We propose that the mechanism by which starch–oil composites provide lubrication to metal surfaces involves the micrometer-sized droplets contained within the dried starch matrix of the composite film that is spray applied to the metal surface. It is reasonable to suppose that a small amount of oil remains on the starch surface after the starch/oil composite is dried, and this surface oil would be proportional to the oil/starch ratio used in the preparation of the composite. The presence of varying amounts of this surface oil could be responsible, at least in part, for the COF results observed. Moreover, pressure on the film surface from the test sled during COF testing could cause additional oil to be released to the coating surface due to rupture of the starch matrix that surrounds the entrained oil droplets. The amount of this additional oil would also be proportional to the initial oil:starch ratio. To test this theory, the 16.4 wt% SBO composite (without sucrose) was spray applied to the surface of several metal specimens and, after drying, the surface of the composite films were gently wiped down repetitively eight times with hexane soaked absorbent towels to remove the SBO on the coating surface. The amount of SBO removed from the coating surface by the hexane was quantified using HPLC analyses and found to decrease to a low constant value indicating the majority of the SBO was removed from the coating's surface (Fig. 5).

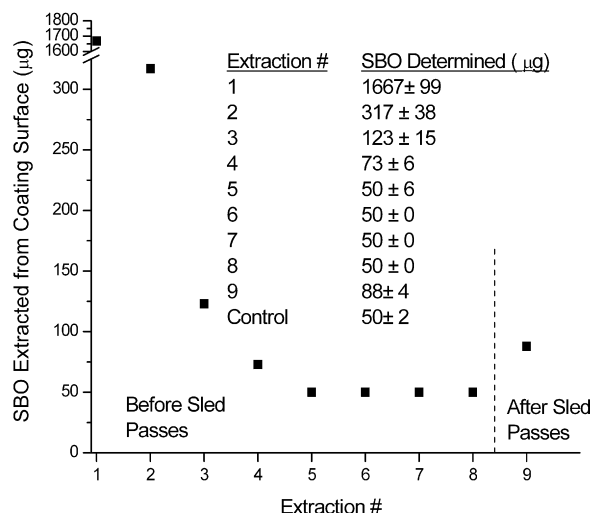


Fig. 5 – HPLC determination of SBO removed by hexane from the surface of dry film lubricant coating that was spray applied to a metal plate. Average of 3 extractions per data point.

These wiped metal plates were then subjected to multiple passes of the COF instrument's two kg sled to examine if oil entrained within the thin starch film would be released to the surface of the film where the steel balls of the sled had contacted the film. Because the thin composite coating contained only a small amount of SBO, multiple sled passes (36 passes × 3 sled balls) were needed to release enough SBO contained in the starch matrix to the coating surface so the SBO could be effectively quantified by HPLC. After multiple sled passes, the surface of the metal plate was again gently wiped down once with a hexane soaked piece of absorbent towel and subsequently analyzed for SBO by HPLC. These experiments showed a small but repeatable increase in the amount of SBO (Fig. 5). The minute amount of oil recovered from the treated specimen (~40 μg) is not surprising considering that with a film thickness of about 16 μm and an estimated scratched area of 2036 mm² (0.16% of total metal plate area), the volume of dried film affected by the sled weight balls was approximately 32.5 mm³. This volume of dried composite would contain at most 5.3 mm³ of SBO (32.5 mm³ × 16.5% oil in the dried composite) having a mass of 4.91 mg of SBO (5.3 mm³ × 0.00092 g/mm³ SBO density) under the sled balls. Although the amount of SBO released by the contact represents only 0.8% of the maximum amount of oil estimated to be within the visible track area left by the test sled, since the balls are spherical, only the center of each track would have borne the entire force of the sled. Therefore, the percentage of oil expressed from the coating may actually be much higher than calculated above.

To ensure the SBO did not migrate to the surface over the time required to run the experiments, the surface oil of a control plate was removed with hexane as for the tested plates but was not subjected to the multiple sled passes to release the SBO. This plate was subsequently wiped down with the other test plates subjected to multiple sled passes and analyzed for surface SBO along with the other plates. The amount

of surface SBO removed from the control plate did not increase showing that the SBO entrapped in the film does not migrate to the surface upon standing (Fig. 5). Interestingly, the COF value for the coated metal plate before hexane extraction was 0.0416 ± 0.001 while immediately after the eight hexane wipe downs the COF value was 0.0670 ± 0.001 . This suggests that while oil on the coating's surface does contribute to the overall reduction in COF, the main source of COF reduction comes from the entrapped oil that is released to the surface at the point of contact thereby providing lubrication on demand.

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